39

THE MAGNETIC BEHAVIOURS OF TITANIUM CAESIUM SULPHATE ALUM

A. BOSE, A. S. CHAKRAVARTY AND R. CHATTERJEE

DEPARTMENT OF MAGNETISM, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA-32

(*Received for publication, June 20, 1959*)

ABSTRACT. A preliminary short account of a new theory for titanium caesium alum is given. The crystalline field in this alum is treated on the molecular orbital method of Stevens and others, as the usual electrostatic field theory is found to fail to explain the magnetic behaviours. It is proposed that the spin-lattice relaxation follows a "Raman Process" at all temperatures between 300°K to 1.2°K. Experimental susceptibility data between 300°K and 100°K as well as the paramagnetic resonance data at 2.5°K can all be accounted satisfactorily by assuming that the trigonal field splitting changes from $-$ 800 cm^{-1} to $-$ 165 cm^{-1}, with temperature, which is also indicated by the large observed increase in the spin-lattice relaxation time from 300°K to 1.2°K.

1. INTRODUCTION

A satisfactory theory of vanadium ammonium alum to explain its magnetic and optical behaviours has been given in a recent paper (1959). The magnetic behaviour of the Ti^{3+} ion in crystals of caesium titanium alum shows certain anomalies, which have not been satisfactorily explained so far. Under the usual cubic and trigonal fields existing in the Ti^{3+} alum (Van Vleck, 1939), the ^2D ground state of the original free Ti^{3+} ion is split up into an orbital triplet and an orbital doublet lying above it with a cubic separation of about 20,000 cm^{-1} (Hartmann and Schlafer, 1951). The triplet is split by the trigonal field into a lowest lying singlet with a doublet above it (Van Vleck, 1939), but the upper doublet (cubic) is not split by the trigonal field and is thus non-magnetic (Bethe, 1929). Each orbital level has a two-fold Kramers spin degeneracy which is removed only by an external magnetic field or by the spin-spin and exchange interactions. As may be expected for such a highly diluted salt, the last two interactions show a spin splitting of only ~ 0.002 cm^{-1} from the adiabatic demagnetisation experiments (Kurti and Simon, 1935). We should thus expect the magnetic susceptibility to obey a Curie law very strictly above $\sim$.003°K upto a temperature at which kT becomes comparable to the trigonal separation Δ, between the lowest orbital singlet and the doublet above it. Unfortunately, the susceptibility data on four different samples of Ti^{3+} alum obtained by Van den Handel (Thesis, 1940) show deviations from Curie law even in the liquid helium range and from one another so wide as to render them quite useless for a theoretical interpretation. The only explanation of the deviations appears to lie in possible

impurities in the samples or chemical decomposition or dehydration of the samples.

The masterly discussions of Van Vleck (1940) show that one has to assume mainly the 'Raman process' as the mechanism of the electron spinlattice relaxation in Ti^{3+} alum at *all* temperatures and that the separation Δ should be of the order of $-1000\ cm^{-1}$, to explain the very short relaxation time $\approx 10^{-7}$ sec. in the liquid air range (Gorter *et al.*, 1938). But at the liquid helium range in order to explain the relaxation time of $\approx 10^{-3}$ sec. (de Haas *et al.*, 1938) Δ has to be taken $\approx -100\ cm^{-1}$. With high magnetic fields in the liquid helium range the 'Direct process' may gain in importance but even that would require Δ to be $\approx -100\ cm^{-1}$.

On the other hand, the experiments on paramagnetic resonance on Ti^{3+} alum, which could be performed only at the helium temperature range, because of the extremely short relaxation times at higher temperatures, yield the values $g_\parallel = 1.25$ and $g_\perp = 1.14$ for the spectroscopic splitting-factors along and perpendicular to the trigonal axis (Bleaney *et al.*, 1955). These g-values could not be fitted on Abragam and Pryces' theory (1951) with any reasonable value of the splitting Δ and the spin-orbit coupling coefficient ζ in the crystal, consistent with the optical absorption value of the cubic splitting $\approx 20{,}000\ cm^{-1}$. Assuming a p-d charge cloud overlap factor $k = 0.7$ following Steven's method (1953), a value of $\Delta \approx -50\ cm^{-1}$ is obtained by Bleaney *et al*, fitting the experimental g-values at helium temperatures, as against Van Vleck's estimate of $-100\ cm^{-1}$.

We have, however, extended Steven's method by assuming anisotropic overlap factors k_z and k_x along and perpendicular to the trigonal axis and obtained the mean susceptibilities fitting to within 2% of the excellent experimental measurements in the range 300° to 100°K of Dutta-Roy (Thesis, 1958) of this laboratory, assuming the following values of the parameters:

$$k_z = 0.800, \qquad k_x = 0.637 \qquad \text{and} \quad \Delta \approx \tfrac{1}{4} - 800\ cm^{-1}$$

$$\zeta_z = 142.6, \qquad \zeta_x = 151$$

which give $g_z = g_\parallel = 1.919$; $g_x = g_y = g_\perp = 1.756$.

These g values and Δ are very different from the resonance values. But it is very interesting to note that with the same values of k's and ζ's the resonance g values can be made to give a good fit (within experimental errors) with $\Delta \approx -165\ cm^{-1}$.

It is interesting to note that the above method of calculation becomes identical with Abragam and Pryce's method in the limit when $k_z = k_x = 1$, and ζ is the same as the free ion value $+154\ cm^{-1}$ and in the range 100°K to 300°K agrees with the experimental susceptibility values to within 5% assuming $\Delta =$

$-1000\ cm^{-1}$. This latter theory, however, cannot give fit with experimental g values at helium temperatures with any reasonable value of Δ and ζ.

It may be remarked that the decrease in spin-lattice relaxation time from $\sim 10^{-7}$ sec. to $\sim 10^{-3}$ sec. with temperature is dependent on the trigonal component of the field which couples the spins of the ground state (though apparently quite free by virtue of the Kramers degeneracy) to the lattice through the spin-orbit interaction, and clearly shows that the trigonal field has considerably decreased at low temperatures. Our two values of Δ at liquid air and liquid helium range are in very satisfactory agreement with the values estimated roughly by Van Vleck from paramagnetic relaxation data.

It is obvious from the above discussions that the trigonal field splitting in Ti^{3+} alum changes drastically from room to liquid helium temperature. The reduction of g-values with temperature indicated above (owing to increase of the negative orbital contributions) shows that the field has become much more symmetric at helium temperature, and also definitely more covalent as shown by the failure of A. & P.'s theory. From the discussions by Van Vleck on the effect of long range fields (1939) we know that in the Ti^{3+} alum the induced distortional effect of the distant atoms on the Jahn-Teller cluster $Ti^{3+}6H_2O$ may be as important as the J.-T. distortional effect itself. Moreover, the above changes in Δ might be easily brought about by changes in the disposition of the H_2O molecules by as small distances as $\sim 10^{-9}$ cm. In the absence of detailed reliable measurements on susceptibility in the range 100°K—1°K we are not able to say whether the change in dispositions takes place continuously as a function of the thermal expansion of the lattice or by a transition of crystal phase of some sort occurring at some intermediate temperatures, either of which might explain the experimental observations on Δ. The effect of thermal expansion is certainly observable from the 2% deviation of the theory from the experimental values even in the liquid air range.

The details will be published shortly elsewhere.

ACKNOWLEDGMENTS

Thanks are due to Mr. S. K. Dutta-Roy of this laboratory for his excellent susceptibility values of Ti^{3+} alum and to Mr. S. Roy for his help in calculations.

REFERENCES

Abragam, A. and Pryce, M. H. L., 1951, *Proc. Roy. Soc.*, **A206**, 173.

Bether, H. 1929, *Ann. der. Physik*, **3**, 133.

Bleaney, B., Bogle, G. S., Cooke, A. H., Duffus, R. J., O'Brian, M. C. M., Stevens, K. W. H., 1955, *Proc. Phys. Soc.*, **A68**, 57.

Chakravarty, A. S., 1959, *Proc. Phys. Soc.* (In Press).

de Haas, W. J., 1938, *Physica*, **5**, 969.
Dutta-Roy, S. K , 1958, D. Phil. Thesis, Calcutta University.
Gorter, C. J , 1938, *Physica*, **5**, 969.
Hartmann, H. von. and Schlafer, H. L., 1951, *Z. Naturf*, **6a**, 760.
Kurti, N. and Simon, F., 1935, *Proc. Roy. Soc.*, A**149**, 152; A**152**, 21.
Stevens, K. W H., 1953, *Proc. Roy. Soc.* A **219**, 542.
Van Vleck, J. H., 1939, *J. Chem. Phys.*, **7**, 61
Van Vleck, J. H., 1940, *Phys. Rev.*, **57**, 426.
Van den Handel, 1940, Thesis, Leiden University.